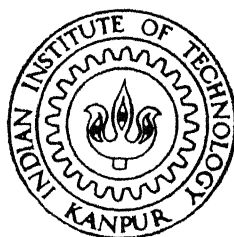# DEVELOPMENT AND CHARACTERISATION OF NICKEL CLADDING ON MEDIUM CARBON STEEL VIA HOT ROLLING

by
VINOD NARANG

DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

APRIL, 1997

DEVELOPMENT AND CHARACTERISATION OF

NICKEL CLADDING ON MEDIUM CARBON STEEL

VIA HOT ROLLING

A Thesis Submitted

in Partial Fulfillment of the Requirements

for the Degree of

MASTER OF TECHNOLOGY

by

VINOD NARANG

to the

DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY
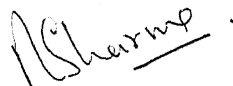
KANPUR

APRIL 1997

CERTIFICATE

This is to certify that the present work, entitled *Development and Characterisation of Nickel Cladding on Medium Carbon Steel via Hot Rolling* by Mr. Vinod Narang has been carried out under my supervision and to my knowledge it has not been submitted elsewhere for a degree.

Dr. R. C. Sharma,

(Professor)

Department of Materials and Metallurgical Engineering,

Indian Institute of Technology,

Kanpur - 208016. India.

dedicated to my parents

ACKNOWLEDGEMENTS

ABSTRACT

In the present work, nickel cladding on a medium carbon steel starting with nickel powder and steel sheet via optimised hot rolling schedule has been obtained. Initially, nickel powder layer of required thickness is placed on roughened steel substrate by three different methods, viz. loosely packed powder, slurry of powder with organic binder, and die compacted powder. This is followed by sintering at 1000^0C for 15 minutes to give green strength to powder layer. The compact thus obtained is hot rolled at 900^0C in 4-7 steps to a total reduction of nearly 65 - 70%. Detailed characterisation of nickel clad steel composite material is carried out using scanning electron microscopy, electron microprobe analysis, microhardness and mechanical testing. Well developed interface and fully densified clad nickel layer, with negligible porosity is observed for all the three cases. Interdiffusion of iron and nickel occurred in approximately 25-100 μm zone in the interfacial region. Strength of the composite material is found to be approximately equal to the weighted average of the strength of constituting materials viz. nickel and steel. Hence, a good clad composite material is obtained by following any of the above mentioned routes.

List of Figures

List of Tables

Contents

CHAPTER 1

Introduction

Clad-metal or Laminated-metal composites consist of two or more layers of different metals or alloys completely bonded to each other. Clad-metal composites having a number of valuable, partly unique properties have assumed ever increasing importance in modern engineering. Individual metals and alloys cannot satisfy any more the ever increasing stringent, complex and often contrasting demands that materials have to meet in regard to strength, corrosion, wear and/or heat resistance, electrical and thermal properties etc. Clad-metal composites can be designed to satisfy different combination of desired properties. They can also be used as substitutes for more expensive alloys. The saving of scarce materials, cost reduction are among the other benefits that are incurred.

The most widely used industrial methods of producing clad composite materials are roll bonding, extrusion, explosive welding, diffusion bonding etc. In recent years such composites are also being increasingly produced by powder metallurgy routes. The various advantages of this route are extensive possibilities of shaping and designing composite material beside the possibility of obtaining 'composite' coatings.

Nickel cladding on carbon steel can be used for applications requiring a combination of corrosion resistance and strength in various industries like chemical, pulp and paper, textile, printing, petroleum, mining, automotive, food machinery industries etc. This composite material takes advantage of the corrosion resistance of nickel while making use of high strength and low cost of carbon steels.

In the present work, cladding of nickel on a medium carbon steel has been carried out via hot rolling. Powder metallurgy techniques have been applied for preplacing nickel powder on steel base. This is followed by a hot rolling schedule. Optimisation and reproducibility of processing route has been established. Detailed characterisation of the composite material by optical and scanning electron microscopy, electron microprobe analysis and mechanical testing has been done.

CHAPTER 2

Literature Review

2.1 Fundamentals of Roll Bonding

Roll bonding, essentially a solid phase welding process came into existence in 1935. It was first applied for the production of compound plates [1]. Major contribution to its development came from Germany and Great Britain. Both cold and hot roll bonding were tried. Since then considerable work has been carried out on roll bonding due to its industrial significance.

Now-a-days, roll bonding is commercially exploited to produce a wide variety of laminated composite materials. Both high temperature as well as room temperature processing has been commercialised. Many factors have been found to effect the quality of the bonds obtained by roll bonding. Achievement of metallurgically sound interfacial bonds is the primary aim of the roll bonding. The various factors affecting bond integrity are summarised below.

Role of Surface Preparation :

When two surfaces come into contact, the actual contact areas are few depending on the surface roughness of the materials. The

3

importance of this parameter can be gauged from a particular study, in which as received sheets of aluminium and copper could not be cold roll bonded due to adsorbed surface contaminants [2]. However, high bond strength was achieved after degreasing and scratch brushing of samples immediately followed by roll bonding. Machined samples were found to give lower bond strength. The rough surfaces leads to increased number of contact points thus enhancing mechanical interlocking. On further deformation excellent bonding is achieved.

Effect of Deformation :

The strength of bond is found to increase with increase in deformation [3]. It has been proposed that a threshold deformation exists for pressure welding, below which no bonding occurs. For aluminium to aluminium roll bonding at room temperature, threshold deformation is reported to be 40% and bond strength has been found to increase rapidly with further deformation and approached the strength of solid metal at about 70% deformation. The threshold deformation is found to depend on nature of metals, temperature of rolling and surface roughness.

Effect of Rolling Temperature :

Increase in rolling temperature is found to result in decreased threshold deformation. It improves the workability of materials thus making it possible to work with wide variety of materials. Room temperature processing is limited to cold workable

materials only. Diffusion of species across interface is also enhanced with increase in temperature, which results in removal of porosity and development of sound metallurgical bond. Some metals dissolve their oxide films at high temperatures, for e.g. iron, copper, titanium etc. In these cases, welding is greatly enhanced at higher temperatures as oxides on the mating surfaces dissolve into the adjacent metal, thus decreasing the area over which bonding is inhibited [3]. Also, the work piece size is limited in cold roll bonding process due to higher rolling load requirement.

Some materials readily form thick oxide layer on surface at higher temperatures, thus greatly retarding the welding process. This can be overcome by use of protective/reducing atmospheres or by use of 'pack' of different material which encases the clad assembly and prevents its contact with atmosphere.

Effect of Metallurgical Variables :

The constituent materials of a specific clad-metal system determine to a large extent the proper processing technique to be followed, the threshold deformation, temperature of working and post heat treatment. Laminated metal composite systems are broadly divided based on the metallurgical nature of the constituents into the following groups :

    (a)   Immiscible pairs [e.g. Pb-Fe, Cd-Fe, Cu-Pb]

    (b)   Completely miscible pairs [e.g. Fe-Ni, Cu-Ni]

    (c)   Partially miscible pairs [e.g. Cu-Ag, Cu-Fe]

    (d)   Intermetallic forming pairs [e.g. Al-Cu, Fe-Al]

Miscible metals were found to weld readily. However, exposure to higher temperature for longer time may weaken the bond due to formation of diffusional porosity in some cases. Immiscible metal pairs and those having limited solubility can also be welded. The bond strength was found to approach the strength of weaker metal at large deformation in such cases [3]. In case of pairs forming intermetallics., the ductility of intermetallic layer exerts great influence on bond properties. Brittleness of this layer above certain critical value of thickness, results in crumbling and splitting apart of the composite.

Effect of Post-Heat Treatment :

In some cases, post heat treatment, i.e. annealing at higher temperatures, may improve the quality of the bond. Effect of post heat treatment depends on the nature of a particular system. If the metallic regions have only partially welded during pressure welding, then they may get completely welded due to diffusion during the post heat treatment. In systems like titanium based alloys which dissolve interfacial oxides, bond strength improves. However, in systems like copper-nickel which are prone to Kirkendall porosity, bond strength disintegrates in proportion to the time spent at a higher temperature. Systems forming intermetallics exhibit varying response i.e. bond integrity may either improve or worsen depending on the nature of intermetallic compound formed and its response to specific heat treatment.

2.2 Choosing a Clad/Substrate Combination

Depending on the end use of the clad composite material various factors like dimensional stability, thermal conductivity, corrosion compatibility, diffusion behaviour etc. of substrate/clad materials should be considered. Apart from the required properties for a certain application, various other considerations in choosing a clad/substrate combination are fabrication compatibility, interdiffusion and metallurgical factors like mutual solubilities, formation of intermetallic compounds etc.

The relative plastic behaviour of clad and substrate material should be considered for fabrication compatibility [4]. If the substrate material is much harder than the clad material, there will be a tendency for substrate to break through the cladding. This is particularly applicable for roll bonding. Melting points of the clad and substrate material should not be too far apart. Otherwise, the hot working temperature of one of the materials may be above the melting point of the other. It may also happen that one of the materials is getting cold worked as working temperature is below its recrystallisation temperature.

Interdiffusion across the interface greatly affects the bond strength. In some cases, the bond strength is a function of diffusion layer thickness and thus optimum bond strength can be attained by controlling its thickness. In some other systems, the diffusion process causes a porous layer to form because of unequal diffusion rates of different elements (Kirkendall effect) . Such

porosity may lead to reduced bond strength, poor heat transfer and high corrosion rate along the interface. When the cladded material is to be used at high temperatures, diffusion process may further continue during service. This may lead to 'contamination' of the clad layer by diffusion of substrate elements, thus resulting in the loss of unique properties of clad layer. This can be prevented by use of an intermediate barrier layer [5].

The phase diagram between substrate and clad material should also be given due importance. In case of completely miscible systems bonding can easily be achieved [3]. In the systems where brittle intermetallic constituents are formed, high temperatures generally leads to faster kinetics of their formation. Working temperature in such cases should be carefully chosen [6]. In completely immiscible systems bonding can be achieved by pressure welding [3].

2.2.1 Interface Strength

The interface between the two materials in contact with each other is very important.It should possess sufficient strength to exhibit its own performance. A sound metallurgical bond existing at interface is necessary to satisfy this requirement. In particular, high strength of the interface is necessary for cladded materials being used for mechanical applications.

The factors affecting the interface strength can be classified into two broad categories, viz. intrinsic factors which are related to the bonding between materials at the atomic level and extrinsic

factors which are related to surface treatment and cladding method followed. Good strength of the interface can be achieved by chemical bonding such as metallic, ionic or covalent bonds, which occurs due to electron transfer across the interface [7]. If the interface is completely flat and clean, the debonding force directly depends on the type of bonding. Surface cleanliness, as emphasised earlier, affects the interface strength as it controls the bonding area of interface. The bonding method followed also affects the interface structure and interface strength. The high temperature prevailing in hot bonding facilitates interdiffusion of elements across the interface as compared to cold bonding.

A practical interface is very difficult to pin-point as it includes macro- and microscopic steps due to surface roughness and due to intermixing, segregation of atoms and formation of intermetallic compounds at the interface. These complexities of practical interface makes it difficult to define a real interface. Thus, it is very difficult to measure the bonding strength of exact interface between two different materials. Usually macroscopic interface strength, which includes the effects of both intrinsic and extrinsic bondings, is measured.

2.3 Roll Bonding of Base Metal with Porous Clad Layer

Roll bonding of base metal with a porous clad layer consists of a suitable powder preplacing technique on prepared base metal surface. Clad layer can either be applied to one side or both sides

of the base metal [8]. This is generally followed by sintering for a short period to impart green strength to compact which also facilitates handling of the compact. Densification of the porous layer and its pressure welding to the substrate is achieved by hot rolling process.

In past, roll bonding was done using both clad and base layer in sheet form. Recently, the powder metallurgy route is gaining lot of research interest particularly in Russia. Among its advantages is the possibility of obtaining composite coatings consisting of more than one metal/alloy. Shaping and designing laminated material with previously specified properties are other advantages [9]. The factors affecting bond integrity as described in Section 2.1, also hold good in this case. But, the use of porous layer imparts certain characteristic features to this processing route. Various powder preplacing methods which have been used are free pouring [9], slurry of powder and binder [10].

Particularly in case of free poured powder on substrate, sintering constitutes an important step. As surface area of loose powder is very large, excess surface energy associated with it acts as a driving force for coalescence of powder particles [11]. Neck formation aided by diffusion and other transport processes takes place and it effectively reduces the surface energy. Grain boundary diffusion has been found to be the controlling step for sintering of porous nickel strip [4]. The porous layer further densifies and shrinks due to removal of pores and develops strength by sintering process. Sintering also helps in interface bonds to develop at the

junction points of porous and solid layers by diffusion processes. If sintering is done after compaction, less shrinkage occurs during sintering due to lower amount of initial porosity. Sintering kinetics is also fast due to increased dislocation population formed during compaction [12].

The full densification of sintered layer and development of interfacial bonds is achieved by hot rolling. The densification and deformation characteristics of porous nickel layer during hot rolling had been studied [13]. Porous layer was prepared by slurry casting and die compaction routes followed by sintering. Hot rolling of porous strip was found to occur in three different stages. In the first stage, rearrangement and restacking of powder particles, depending on their size distribution, occurred without any longitudinal flow. Second stage showed a continuous increase in interparticle area with longitudinal flow of strip. Interconnected porosity changed to isolated porosity, which got removed by pore fragmentation and collapse of porosity. Third stage marked the disappearance of original particle boundaries and virtually all porosity was removed. Longitudinal flow increased rapidly with deformation.

For roll bonding of porous layer with a solid base the densification process in porous layer as described above operates besides the development of bonds at the interface. During rolling, only when the density of porous layer approaches a critical density value, both layers begin to deform simultaneously [14]. The critical density is dependent on the shear yield stresses of solid

and porous layer, and on the relative thickness of porous and solid layer.

2.3.1 Model of Roll Cladding Process

I.I.Renne has estimated the rolling parameters of two layer strip containing a porous layer and a solid layer using mathematical model [14, 15]. Rigid bonding of porous layer to solid layer was assumed. The simultaneous plastic flow of both layers occurs when pressure exerted by the rolls on compact satisfies condition of plasticity of solid and porous materials given by,

$$T (s) = K (s) \qquad\qquad (1)$$

$$T^2 (p) + \alpha . \sigma^2 (p) = \delta K^2 (p) \qquad\qquad (2)$$

where, T (s) & T (p) are the intensities of tangential stresses acting in solid and porous layer, respectively ; σ (p) is the mean stress acting in porous layer ; K (s) & K (p) are pure shear yield stress of solid and porous layer, respectively ; α & δ are the functions of relative density of porous layer.

For conditions 1 & 2 to be satisfied simultaneously, starting relative density of porous layer τ_0 should exceed some limiting value, τ_1 . When $\tau_0 < \tau_1$, the solid layer experiences no plastic deformation and overall deformation of the compact takes place only as a result of densification of porous layer. Only when $\tau_0 \geq \tau_1$, both layers simultaneously participate in plastic flow.

For the first case of $\tau_0 < \tau_1$, stressed state in the porous

12

layer of the compact being rolled without elongation can be described in same way as the stressed state in a porous compact undergoing uniaxial densification in a rigid die, which is given as,

$$\sigma_y (p) = -2\sqrt{3}/3 . K (p) . \tau_x^{3/2} . (1 - \tau_x)^{-1/2} \qquad (3)$$

$$\sigma_x (p) = -\sqrt{3}/3 . K (p) . \tau_x^{3/2} . (1 - \tau_x)^{-1/2} . (3\tau_x - 1) \qquad (4)$$

where, $\sigma_y (p)$ & $\sigma_x (p)$ are the longitudinal stress components for porous layer. τ_x is the relative density of porous layer.

For the second case, when whole of the compact experiences plastic flow, the longitudinal stress is given as,

$$\sigma_x = \beta_x . \sigma_x (p) + (1 - \beta_x) . \sigma_x (s) \qquad (5)$$

where, $\beta_x = h_x (p) / h_x$ is a parameter determining the position of boundary between the layers ; $h_x (p)$ & h_x are the thickness of porous layer and compact respectively.

For determining the limiting density of porous layer, τ_1 the expression,

$$\sqrt{3}/3 (1 - \tau_0) . K . \tau_1^{3/2} . (1 - \tau_1)^{-1/2} . \{ [3\tau_0 . \beta_0 +$$
$$2 (1 - \beta_0)] . \tau_1 - \tau_0 . \beta_0 \} - 2 = 0 \qquad (6)$$

has been obtained. Where, $K = K (p) / K (s)$ and β_0 is the position

13

of boundary in the starting strip.

K parameter has been found to strongly influence the τ_1 value. When yield stress of solid layer increases as compared to porous layer, τ_1 is found to increase. Under certain conditions, like at sufficiently large value of K, preferential deformation of the solid layer may take place during rolling, and the porous layer may practically experience no densification i.e. behave like an incompressible solid.

For determining the relative compression of the compact, ϵ_1 when τ_1 is attained, the expression,

$$\epsilon_1 = \beta_0 . (1 - \tau_0 / \tau_1) \tag{7}$$

has been obtained. The factor ϵ_1 is affected most by factor β_0 thus stating the importance of ratio between thickness of porous and solid layer in the starting compact. When $\tau_0 < \tau_1$ and relative compression of the compact $\epsilon < \epsilon_1$, the deformation of compact during rolling consists only in plastic uniaxial densification of the porous layer, with the solid layer behaving like an undeformable solid, and the compact experiences no elongation. Thus, rolling of two layer solid/porous compact depends to a large extent on the flow characteristics of the porous and solid layer materials and also on the ratio of thicknesses of the two layers in the starting compact.

14

2.4 Nickel Cladding on Steels

Cladding of nickel and its alloys to steel base has generated considerable research interest. Its potential· industrial applicability for corrosion resistance and strength applications is immense. Nickel layer provides corrosion resistance while steel base provides strength and toughness to the composite material.

An excellent study of nickel alloys viz. Inconel and Hastealloy cladded to AISI 4130 steel via hot pressing and hot isostatic pressing has been reported [16]. Hot pressing of discs of substrate and clad assembly was carried out at 1050^0C for 1h at a pressure of 34 MPa in inert atmosphere. HIPing was carried out at 1150^0C under a pressure of 200 MPa.

Detailed microstructural analysis was done to characterise the clad material. The microstructure of base steel was found to depend on cooling rate after bonding. Close to the interface on the steel side, a higher percentage of ferrite was observed as compared to the bulk steel, indicating decarburisation of steel. A thin region, around 4-12μm thick, of austenite was found parallel to the interface on steel side. The width of this band was in direct proportion to bonding temperature and time. The existence of this band was attributed to stabalisation of austenite due to diffusion of nickel and chromium to steel side. This band was free of carbide precipitates.

The microstructure of clad region near to interface region consisted of precipitated carbides. The precipitation was observed

15

on twins and grain boundaries. The width of this region was found to increase with increase in processing temperature and time. Majority of carbides were identified as $M_{23}C_6$ type. M_7C_3 carbides close to interface were also observed. M_7C_3 carbide precipitation is favoured by high concentration of carbon and low concentration of chromium. Since close to interface, high concentration of carbon diffused from steel and loss of chromium to steel was there, these type of carbides were observed. At larger distances from interface, precipitates were found primarily at grain boundaries thereby indicating the rapid grain boundary diffusion. Precipitated region extended upto a zone of 100-150 μm. The bulk microstructure of clad material consisted of equiaxed austenitic grains.

The concentration profiles of various elements close to interface was also determined using energy dispersive spectroscopy. Interdiffusion of elements in 20-30 **μm zone** was observed. Chromium diffused to longer distances as compared with other elements. Nickel showed a steeper change in composition at the interface. Longer processing temperature and time resulted in thicker interdiffusion zone.

Roll bonding of iron and nickel plates has also been tried [3]. The plates were degreased in trichloroethylene vapour, scratch brushed and pinned at the corners with rivets. Rolling was carried out at 920°C to a total deformation of 56%. The bond strength was found to be 17tons/sq. in., which is nearly equal to the strength of iron. On subsequent post heat treatment in hydrogen for 3hr at 1250°C the bond strength reduced to half this value. This was

16

attributed to formation of diffusional porosity.

However in another study, pressure welding of iron to nickel plates after proper surface treatment resulted in slight adherence only [17]. The plates were deformed to 72%. Since in this case high temperature was not applied, metallurgical bond was unable to form.

2.5 Aim of the Present Work

Nickel cladded steel composite material finds extensive uses for corrosion resistance applications. The clad nickel layer provides corrosion resistance and the steel base provides strength and toughness. In past, roll bonding of nickel and steel sheets has been successfully obtained [3]. The successful bonding of nickel alloys to low alloy steel using hot pressing, hot isostatic pressing has also been reported [16].

In the present work, cladding of nickel on a medium carbon steel has been studied by using nickel powder as clad layer and steel sheet as substrate. The main aims of this work are ,
i) To develop nickel cladding on medium carbon steel using the clad layer in porous form. Optimisation of processing route consisting of powder preplacing, sintering and hot rolling.
ii) To characterise the resulting clad composite material particularly in the interfacial region.

17

CHAPTER 3

Experimental Details

The experimental procedure to obtain a nickel cladded steel composite material consists of nickel powder preplacing on roughened steel substrate by three different methods followed by sintering and hot densification rolling. The flowsheet consisting of various processing steps involved is shown in Figure 1. A detailed description of the processing steps followed is given in the following sections.

3.1 Preparation of Specimens

The starting materials used for present work were in form of hot rolled sheet of AISI 1040 steel and carbonyl nickel powder. Nickel powder was obtained from Semi-Elements Inc., a US firm. The spherical shaped nickel powder was in size range 90-130 μm. The nominal composition of steel and nickel powder as determined by chemical analysis and electron probe microanalysis, respectively, is given in Table 1. As a first step, steel strips of dimensions 20mm X 50 mm were cut and machined down to 4 - 9mm thickness range. The top oxide layer was also removed during machining. A perpendicular hole with opening in the bottom face was drilled to facilitate hot rolling. The top surface of steel strip to be
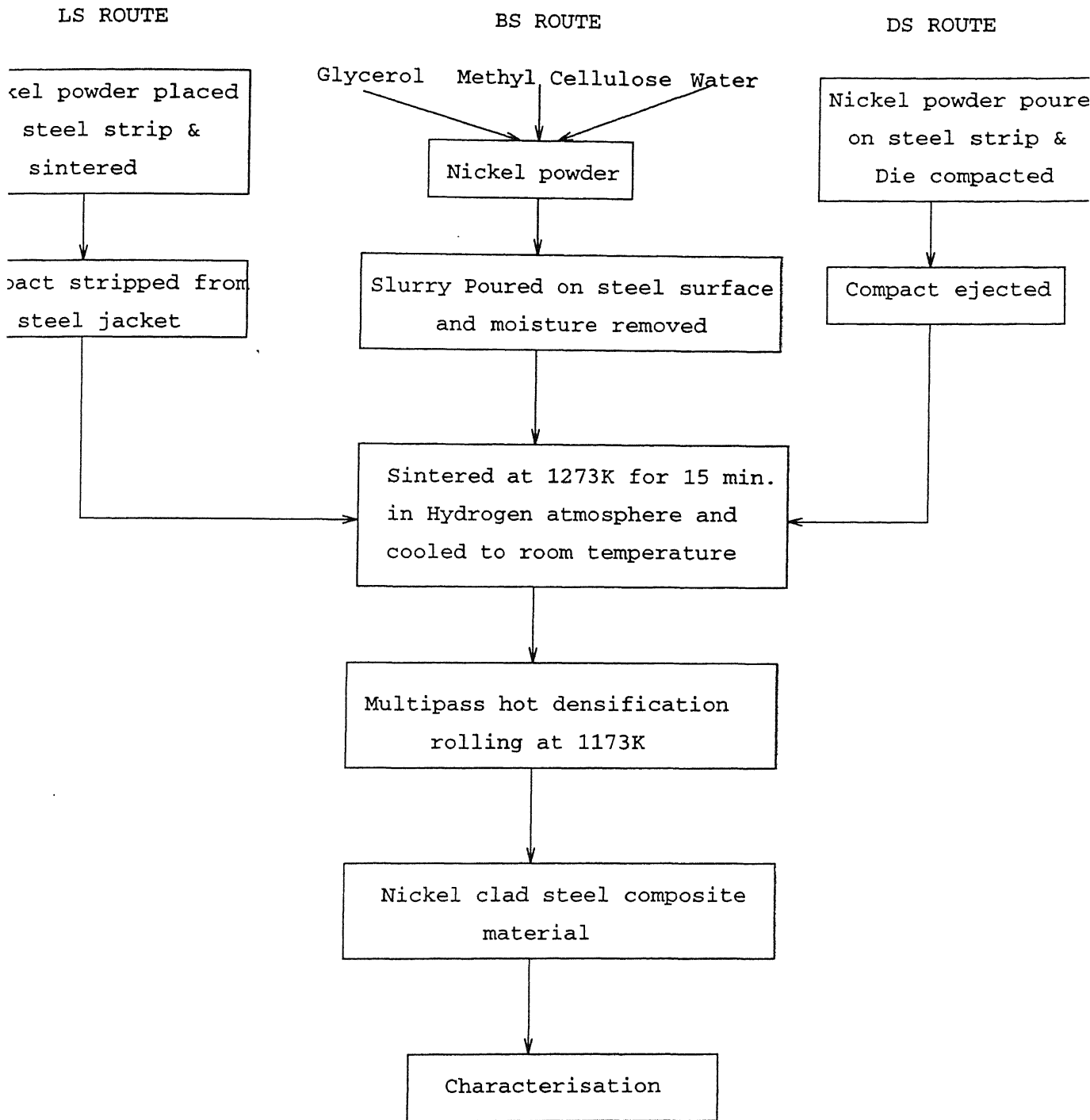
LS ROUTE   BS ROUTE   DS ROUTE

Glycerol   Methyl Cellulose   Water

```
┌─────────────────┐      ┌─────────────────┐      ┌─────────────────┐
│ kel powder placed│      │  Nickel powder  │      │Nickel powder poure│
│  steel strip &   │      └─────────────────┘      │ on steel strip & │
│    sintered      │                               │  Die compacted   │
└─────────────────┘                                └─────────────────┘
        │                         │                         │
        ▼                         ▼                         ▼
┌─────────────────┐      ┌─────────────────────────┐  ┌─────────────────┐
│ act stripped from│      │Slurry Poured on steel surface│ Compact ejected │
│   steel jacket   │      │  and moisture removed   │  └─────────────────┘
└─────────────────┘      └─────────────────────────┘          │
        │                         │                            │
        │                         ▼                            │
        │       ┌──────────────────────────────────┐          │
        └──────▶│ Sintered at 1273K for 15 min.     │◀─────────┘
                │ in Hydrogen atmosphere and        │
                │ cooled to room temperature        │
                └──────────────────────────────────┘
                                │
                                ▼
                ┌──────────────────────────────────┐
                │ Multipass hot densification       │
                │        rolling at 1173K           │
                └──────────────────────────────────┘
                                │
                                ▼
                ┌──────────────────────────────────┐
                │ Nickel clad steel composite       │
                │            material               │
                └──────────────────────────────────┘
                                │
                                ▼
                       ┌─────────────────┐
                       │ Characterisation│
                       └─────────────────┘
```

Figure 1: Various steps involved in the Processing of Nickel Clad
Steel Composite Material

Table 3.1 : Nominal Compositions of Materials Used

Element	AISI 1040 Steel[*]	Nickel Powder[*]
Carbon	0.4	...
Silicon	0.12	...
Manganese	0.08	...
Sulphur	0.04	...
Iron	Bal.	0.2098
Copper	...	0.0438
Nickel	...	Bal.

* With minor amount of other elements.

cladded was cleaned using acetone. Then the surface was made rough using a coarse file to promote mechanical engagement of powder with the steel surface. To prevent any contamination of the prepared surface, immediately after its preparation, nickel powder using three different preplacing techniques was placed on the steel surface.

3.2 Nickel Powder Preplacing Techniques

3.2.1 As Loose Powder

A steel jacket of dimensions 100 X 50 X 10 mm with a rectangular hole was designed. This was made to shape loose powder on steel surface. First the inner walls of jacket were given graphite wash to prevent sintering of powder with the steel wall. Then the steel sheet was placed inside jacket and on prepared surface powder was free poured and levelled to required thickness.

3.2.2 Using an Organic Binder

In this technique, nickel powder was mixed thoroughly with methyl cellulose binder. Glycerol and water additions were done to obtain a proper slurry. The optimised binder content was found to be 1% of powder weight. The slurry was poured on prepared steel surface and levelled to required thickness. Removal of moisture before sintering was done at 100^0C for 30 minutes.

3.2.3 As Die Compacted Layer

In this technique, steel strip of dimensions 30 X 18 X 3.8 mm was placed in rectangular die. Nickel powder was poured on prepared steel surface and compaction was done under a pressure of 250 kg/cm^2. Maximum pressure was applied for a holding time of 2 minutes. Compact was then ejected from the die.

3.3 Sintering

Sintering of the two layer strip prepared by above mentioned techniques was done to develop green strength in the powder layer. It also helped in development of interfacial bonds at contact junctions of porous and solid layers. The powder preplaced by loose powder technique was first sintered at 1000°C for 20 minutes in graphite powder bed to facilitate handling of the compact. After cooling to room temperature in the same bed, compact was stripped from the steel jacket.

Sintering of all the compacts obtained by different techniques, was done in H_2 gas atmosphere at 1000°C for 15 minutes followed by cooling to room temperature in the same atmosphere. The ratio of nickel layer to steel layer thickness was in the range 0.3-0.4 . This was determined by taking into account that interface is to be protected from oxidation during processing and also peeling-off of the nickel layer is to be avoided during multipass hot rolling. Small samples were cut after sintering and were kept for characterisation. The samples have been designated as LS i.e. Loose Sintered , BS i.e. Bindered Sintered and DS i.e. Die compacted & Sintered as obtained by loose powder, use of organic binder and die compacted powder techniques, respectively.

3.4 Hot Rolling

Hot rolling was carried out for all the compacts to densify the porous nickel layer and develop good interfacial strength. Heating of the compacts was done at a temperature of 900°C for 10 minutes in protective Argon gas atmosphere. The heating temperature being well above the recrystallisation temperature of steel and

nickel. The furnace used was horizontal tube inconel furnace. It was closed from one end and there was provision for maintaining a protective gas atmosphere. Spiral silicon carbide heating elements were used. The furnace was first calibrated and constant temperature zone was also determined.

The experimental set up for hot rolling is shown in Figure 2. A thin nichrome wire was tied to steel through previously drilled hole. Rolling was carried out on a Two - High rolling mill having 135mm diameter rolls rotating at a speed of 55 r.p.m. The heating furnace was interlinked with the rolling mill in such a manner that the sample remained in protective argon atmosphere up to the nip of the rolls. Required roll gap was set manually. Thickness reduction was carried out by pulling the wire attached to sample and forcing the sample between the rolls. Immediately, after hot rolling sample was put in graphite powder bed to prevent oxidation. After each rolling pass, cracked edges were sheared off and small samples were cut for characterisation. Hot rolling was carried out in subsequent passes in the same manner till a fully dense clad composite material was obtained.

3.5 Characterisation Methods

3.5.1 Scanning Electron Microscopy (SEM)

JEOL JSM 840A, Scanning electron microscope was used to observe powder morphology, grain size of nickel in clad layer, microstructure of hot rolled samples particularly in the interfacial region and fractured surface of tensile loaded samples. Mounted samples were used for SEM study. Cold setting resin with hardener was used for mounting purpose. The sample preparation
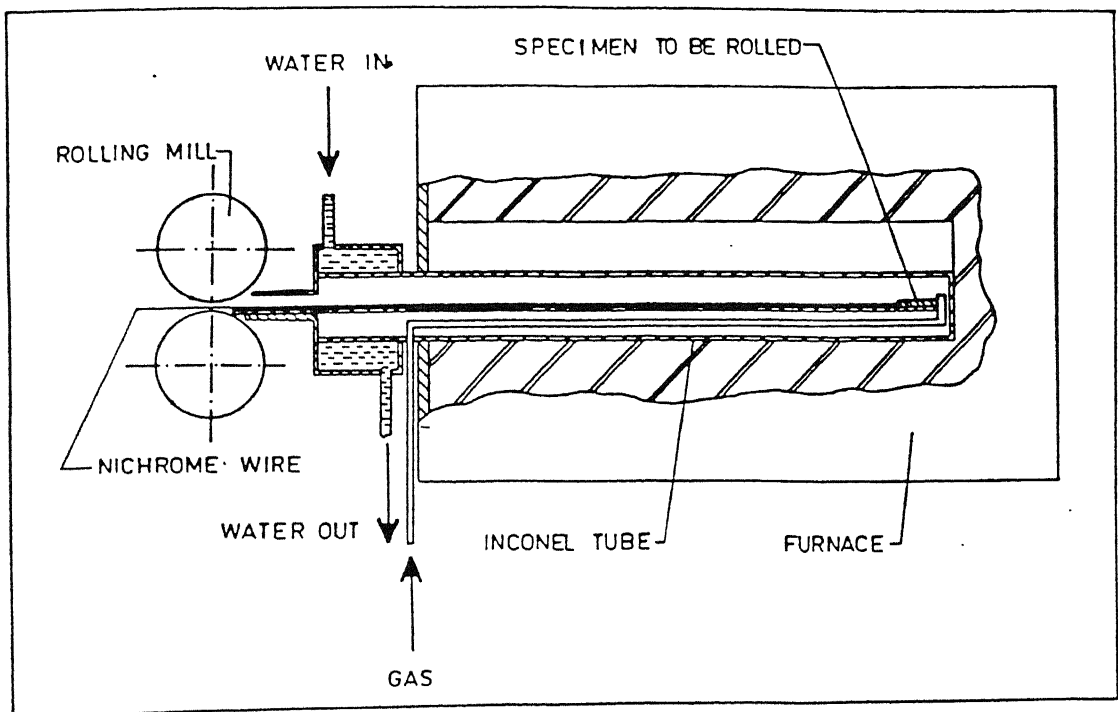
Figure 2 : Experimental Set Up for Hot Rolling.

24

consisted of polishing on various successive grades of emery paper down to 4/0 grade followed by fine cloth wheel polishing with an alumina powder suspension. Acetone wash followed by proper etching was done to reveal the microstructure. For etching steel, 2% nital etchant was used. Merica's reagent having equal volumes of nitric acid and acetic acid was used to etch clad nickel layer. Etching time was kept at 5 - 10 seconds. Rolling direction along the thickness of rolled samples was kept as direction of observation.

3.5.2 Electron Probe Micro Analysis (EPMA)

JEOL JXA-8600, Electron probe micro analyser was used to determine the extent of interdiffusion of iron and nickel at the transition zone close to cladded interface and also to determine the composition of nickel powder. The mounted and etched samples prepared for SEM were also used for EPMA studies.

3.5.3 Microhardness Testing

Microhardness of samples was measured using Leitz Miniload Microhardness Tester, which gives microhardness in Vicker's Hardness Number (VHN). Microhardness profiles for clad nickel layer with increasing percentage reduction and in region on either side of interface for fully densified samples were determined. Load of 50g was used for indentation and VHN was then calculated using the formula,

$$VHN = 1.854P/d^2$$

where, P is the applied load in Kgs. and d is the diagonal of

indentation impression in mm. The mounted and etched samples prepared for SEM were also used for microhardness testing.

3.5.4   Mechanical Testing

The overall macroscopic strength of cladded samples was evaluated using Tensile Test on INSTRON machine. Steel sample was also tested. Samples were annealed at 900^0C for 15 minutes to get a homogenous structure. These were prepared for tensile test with standard dimensions. Full scale load of 10kN, cross head and chart speed of 0.5mm/sec and 20mm/sec, respectively were used as parameters for testing. The various mechanical properties determined were percentage elongation, yield strength and ultimate yield strength.

The nature of fracture of tensile loaded samples was studied using SEM. Particular attention was given to the interfacial region. The samples fractured during tensile test were used in this case without any surface preparation or etching.

CHAPTER 4

Results and Discussion

4.1   Hot Rolling Data and Analysis

Initially, various hot rolling schedules were tried for samples prepared by different methods. This was done to optimise the rolling schedule. For LS and BS samples, reduction in the first pass in excess of 15% resulted in delamination. However, in the subsequent passes reduction of the order of 20-30% could be given. For DS sample, higher reduction, of the order of 20-30%, was possible for the first as well as subsequent passes. Due to rolling mill load limitation higher reduction passes could not be tried. Manual roll gap setting prevented giving accurate reduction passes. Hot rolling parameters for LS, BS and DS samples, that were finally used, are given in Tables 2, 3 and 4, respectively. Here, 'h' & 'H' refers to initial and final compact thickness, respectively, and 'r' & 'R' refers to percentage reduction for a given pass and total % reduction upto that pass, respectively.

The first rolling pass is more critical in case of LS (Loose Sintered) and BS (Bindered Sintered) samples, because of their high initial porosity. These samples had porosity levels of nearly 60-70% as inferred from scanning electron micrographs (see Figs. 4 (a) & 5 (a)). The first rolling pass should also provide sufficient

Table 2 : Rolling Parameters for LS Sample

PASS	h (mm)	H (mm)	r (%)	R (%)
1	5.7	5.0	12%	12%
2	5.0	4.42	12%	23%
3	4.42	3.8	14%	33%
4	3.8	3.0	21%	47%
5	3.0	2.26	25%	60%
6	2.26	2.0	12%	65%

Table 3 : Rolling Parameters for BS Sample

PASS	h (mm)	H (mm)	r (%)	R (%)
1	11.84	11.0	7%	7%
2	11.0	9.38	15%	21%
3	9.38	8.46	10%	29%
4	8.46	7.56	11%	36%
5	7.56	6.28	17%	47%
6	6.28	4.52	28%	62%
7	4.52	3.44	24%	71%

Table 4 : Rolling Parameters for DS Sample

PASS	h (mm)	H (mm)	r (%)	R (%)
1	5.3	3.9	26%	26%
2	3.9	3.02	23%	43%
3	3.02	2.36	22%	56%
4	2.36	1.6	32%	70%

bonding of nickel layer to the steel substrate. In the initial reduction passes, predominantly densification of the porous layer occurs, with very little deformation of the substrate. Only after densification of the porous layer has occurred to certain extent, both layers begin to experience plastic flow simultaneously [12]. The nickel layer peeled off from the steel base when percentage reduction exceeded about 12 - 15% in the first reduction pass in case of LS and BS samples. This was probably due to very little initial bonding at interface and insufficient strength of the porous nickel layer. As the nickel layer densified and interfacial bond developed, 20-30% reduction was possible in subsequent passes, without any problems. Total reduction of 65% & 71% was given to LS & BS samples, respectively. This was found to be sufficient for densification of nickel layer and development of good interface with negligible porosity.

In case of DS (Die compacted & Sintered) sample, higher reduction of the order of 25-30% was possible even in the first pass, without delamination of the nickel layer. In this case, die compaction resulted in densification of the nickel powder layer. Some cold welding of the powder with rough surface of steel may also had occurred. This resulted in increase in contact area between nickel and steel layers. The following step of sintering further caused densification of the compacted nickel layer. Strengthening of interface bonds due to diffusion bonding at the contact areas also occurred. Thus, due to dense nickel layer and partly developed interface bonding higher deformation was possible

31

even in the first pass as compared from LS & BS sample. After die compaction, the porosity level in nickel layer of DS sample was 32%, as calculated by weight and volume measurements. DS sample was given a total reduction of 70% and this was found to be sufficient for obtaining a good clad composite material.

Table 5 gives the relative reduction in thickness of steel and nickel layer for the various samples during hot rolling. For LS sample, a total reduction of 71% for the compact resulted in 57% reduction of steel substrate, while nickel layer reduced by 91%. Similar results were obtained for BS sample also. Part of the reduction in thickness of the nickel layer was due to densification of the initially porous layer. The nickel layer of DS sample had reduced to lesser extent as compared to LS and BS samples (see Table 5), as it initially had lower porosity.

4.2 Microstructural Evaluation

Nickel powder size and morphology, as observed in SEM, is shown in Fig. 3 (a) & (b). Nickel powder is in size range 90-130μm. It has predominantly spherical shape as expected for carbonyl nickel powder.

Microstructures of LS sample after sintering and reduction of 12%, 47% and 65% is shown in Fig. 4 (a), (b), (c) & (d), respectively. Initial porous nature of interface is evident, as observed from Fig. 4 (a). The spherical nickel powder particles in contact with each other at some places are clearly seen. The

Table 5 : Relative Reduction in Thickness of Nickel and Steel
Layers during Hot Rolling

Sample	LS		BS		DS	
	Steel	Ni	Steel	Ni	Steel	Ni
Initial Thickness (mm)	4.38	1.32	9.10	2.74	3.8	1.5
Final Thickness (mm)	1.88	0.120	3.19	0.250	1.28	0.320
% Reduction of the layers	57%	91%	65%	91%	66%	79%
Composite % Reduction	71%		65%		70%	

\
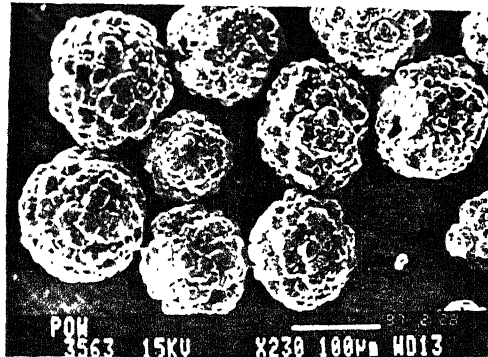
(a)
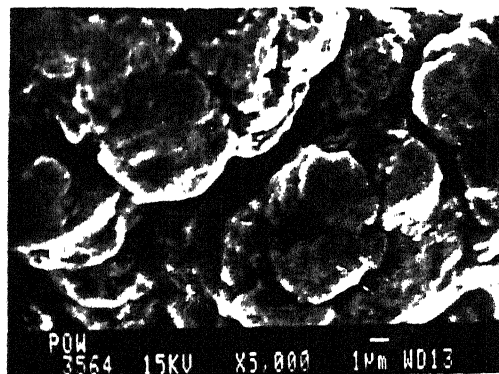
(b)

Figure 3 : SEM micrograph of Nickel Powder (a) 230 X, (b) 5000 X.

34
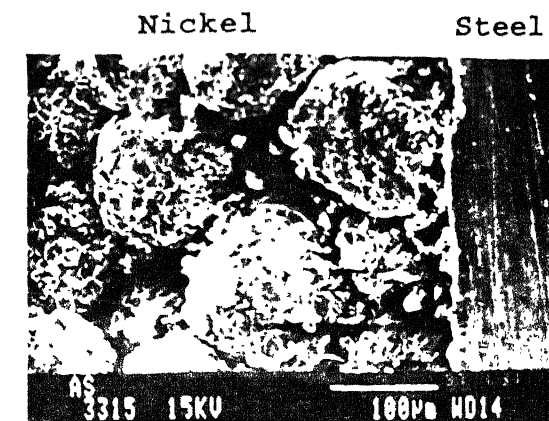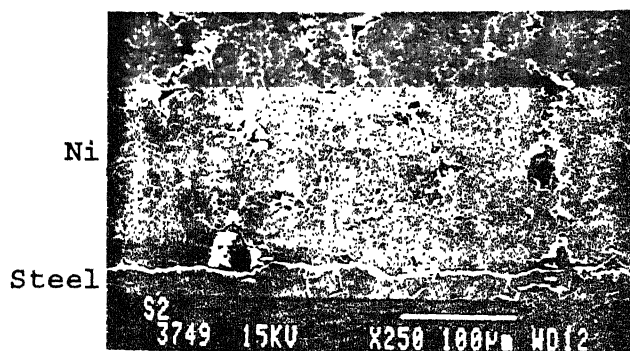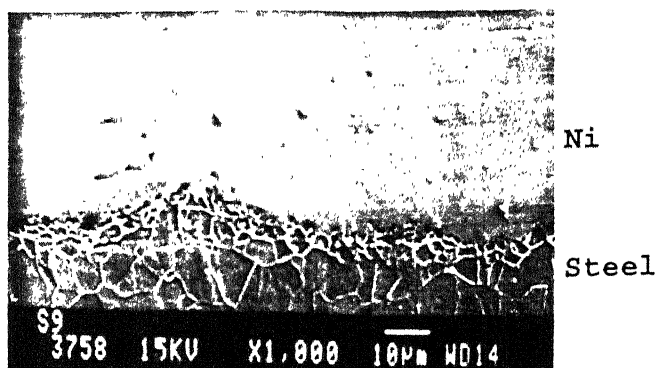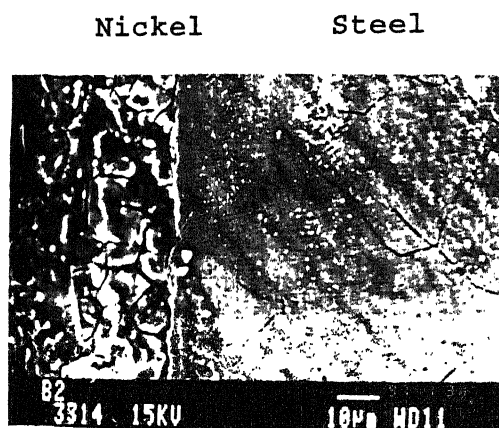
Figure 4 : SEM Micrographs of LS sample (a) After sintering; and After (b) 12%, (c) 47% , & (d) 65% reduction. (b) & (c) Nital etched, (d) Merica's Reagent etched.

35

porosity level after sintering is around 60-70%, as observed from micrograph. With hot reduction, decreasing amount of porosity both in nickel layer as well as at the interface is observed, as seenfrom Fig. 4 (b), (c), & (d). Well developed interface and fully densified nickel layer with virtually no porosity are observed for the sample after final rolling pass, as seen from Fig. 4 (d).

Micrographs of BS sample after sintering and after 7%, 21%, 29%, 47% and 71% reduction are shown in Fig. 5 (a), (b), (c), (d), (e), & (f), respectively. The evolving microstructure of nickel claded steel composite material is evident. The microstructures are similar to LS sample. Well developed granular structure of clad nickel layer is observed from Fig. 5 (f). Average grain size of nickel is found to be 24 μm.

Fig. 6 (a), (b), (c) & (d) show the microstructure of DS sample after Die compaction, and after 26%, 56% & 70% deformation, respectively. Die compaction resulted in deformation of powder particles and substantial reduction in porosity, as observed from Fig. 6 (a). With increasing deformation, further reduction in porosity of the nickel layer occurred and porosity free interface developed between nickel layer and the steel substrate, as observed from Fig. 6 (b), (c), & (d).

Although the porosity levels after sintering, in case of LS and BS samples are high as compared to DS sample, the microstructure of all the samples after 65 to 70% hot deformation is nearly similar. Thus, irrespective of the powder preplacing technique and initial level of porosity, a well defined, sharp,
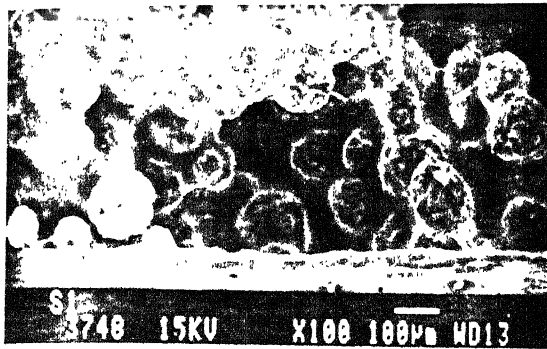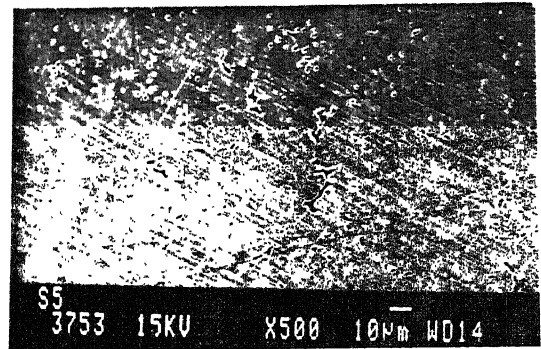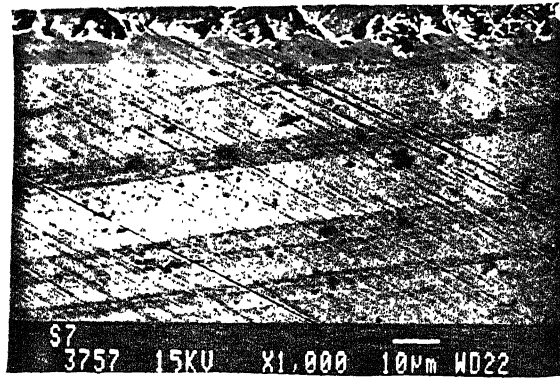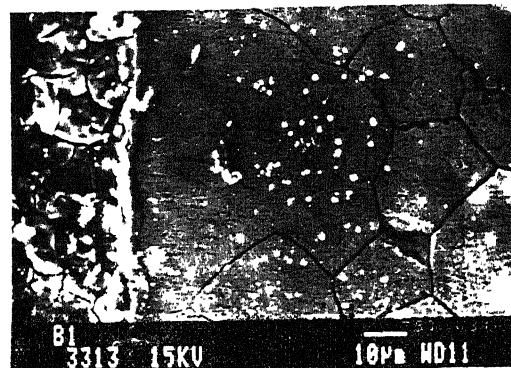
(a)
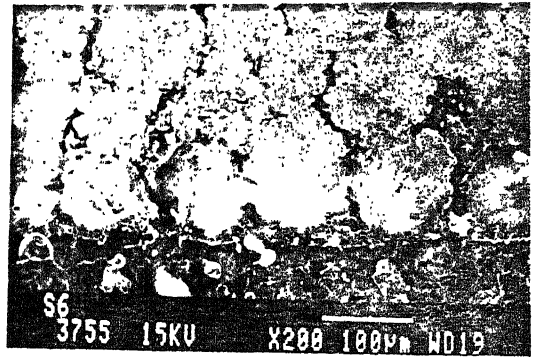
(b)

(b)

(d)

Figure 5 : SEM Micrographs of BS sample (a) After Sintering; and After (b) 7%, (c) 21%, (d) 29%, (e) 47% & (f) 71% Reduction.
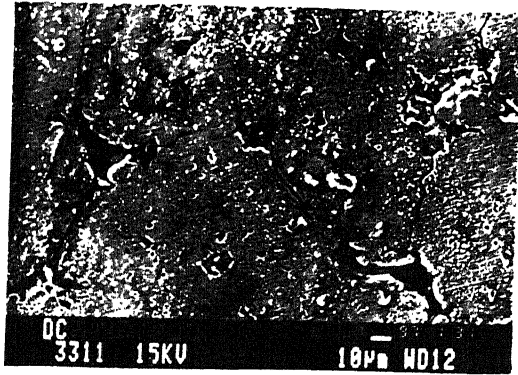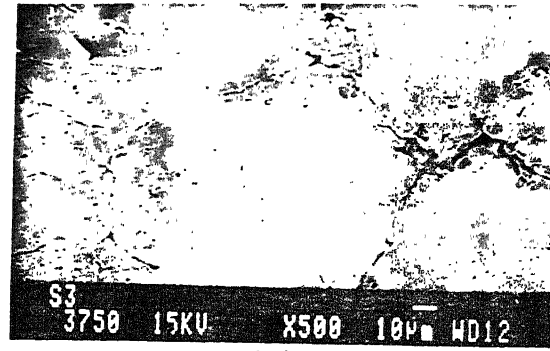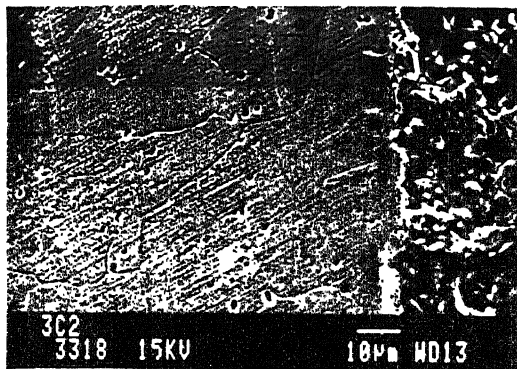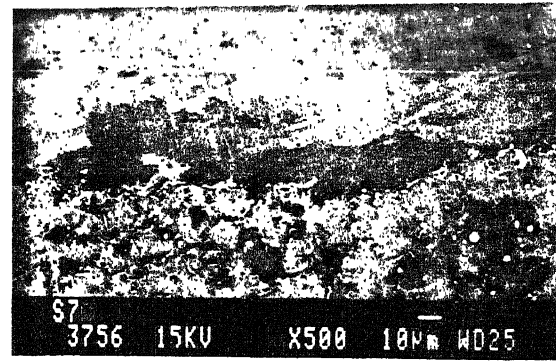
(e)

(f)

Fig. 5 Contd.

(a)

(b)

(c)

(d)

Figure 6 :   SEM Micrographs of DS sample (a) After Die compaction;

and After (b) 26%, (c) 56%, & (d) 70% deformation.

uncontaminated interface between steel and nickel is obtained after final deformation. Interfacial defects like microcracking, cooling cavities etc. are not been observed. Hence, it may be said that, from microscopic viewpoint a good "Metallurgical Bond" has been achieved in all the cases.

4.3 Interdiffusion at the Interface

The concentration profiles of iron and nickel across the interface were determined by EPMA in the fully hot rolled samples. The results for LS, BS and DS samples are shown in Figures 7, 8 and 9, respectively.

For LS and BS samples significant interdiffusion of Fe and Ni has occurred in the 25-40 μm zone at the interface, as observed from Figs. 7 & 8. Iron has diffused to a relatively longer distance into clad nickel layer as compared to diffusion of nickel into the steel substrate. Diffusion of nickel into iron occured by matrix diffusion, whereas diffusion of iron into the nickel layer may have predominantly taken by grain boundary and surface diffusion. Grain boundary and surface diffusivities are generally orders of magnitude higher than matrix diffusivity. Hence, more penetration of iron into nickel layer.

For DS sample interdiffusion zone is of the order of 100μm thickness, as observed from Fig. 9. Iron has diffused to a zone of nearly 80μm thickness into clad nickel layer. In this case, die
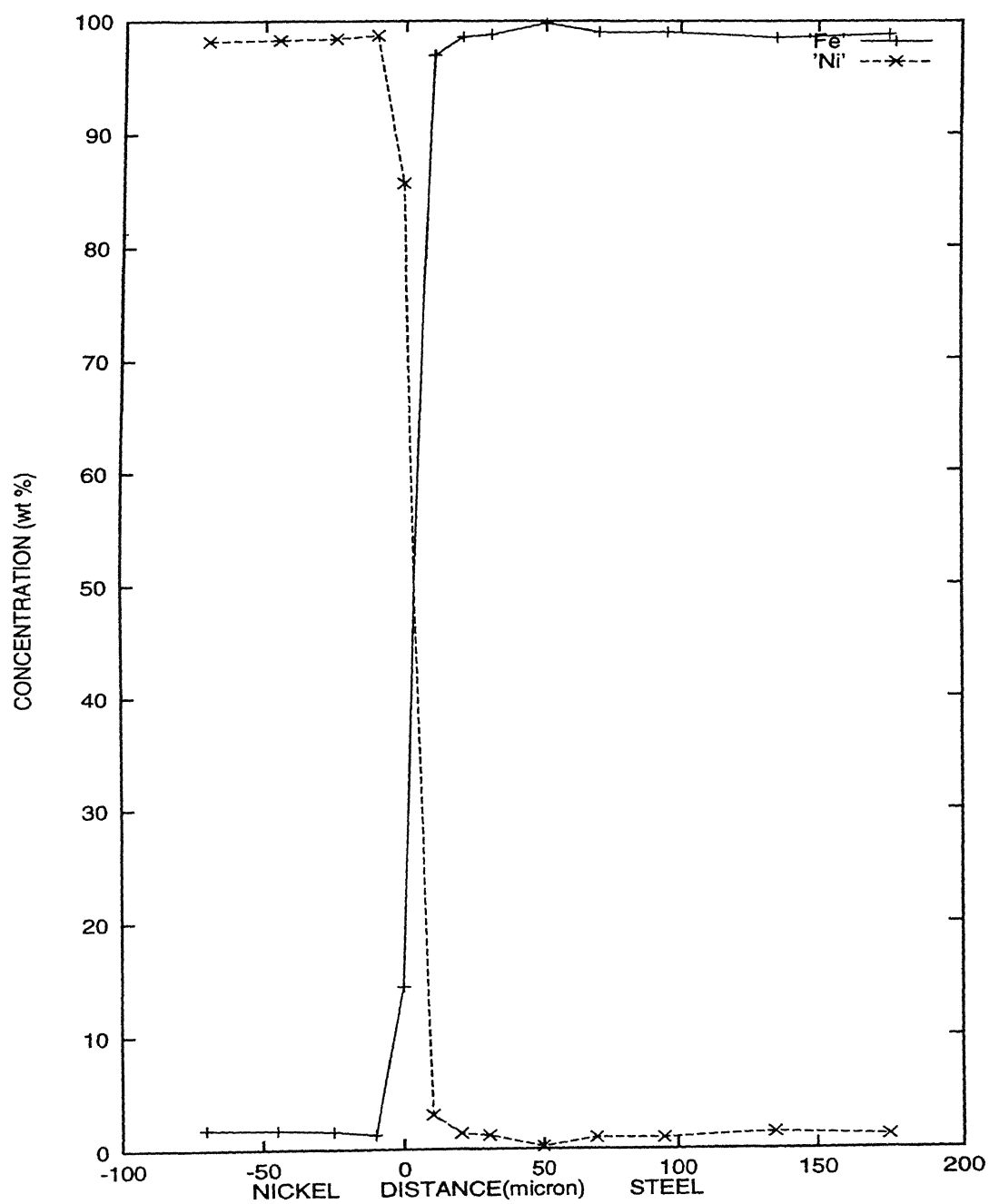
Figure 7: Concentration profile of LS Sample in the Interfacial Region
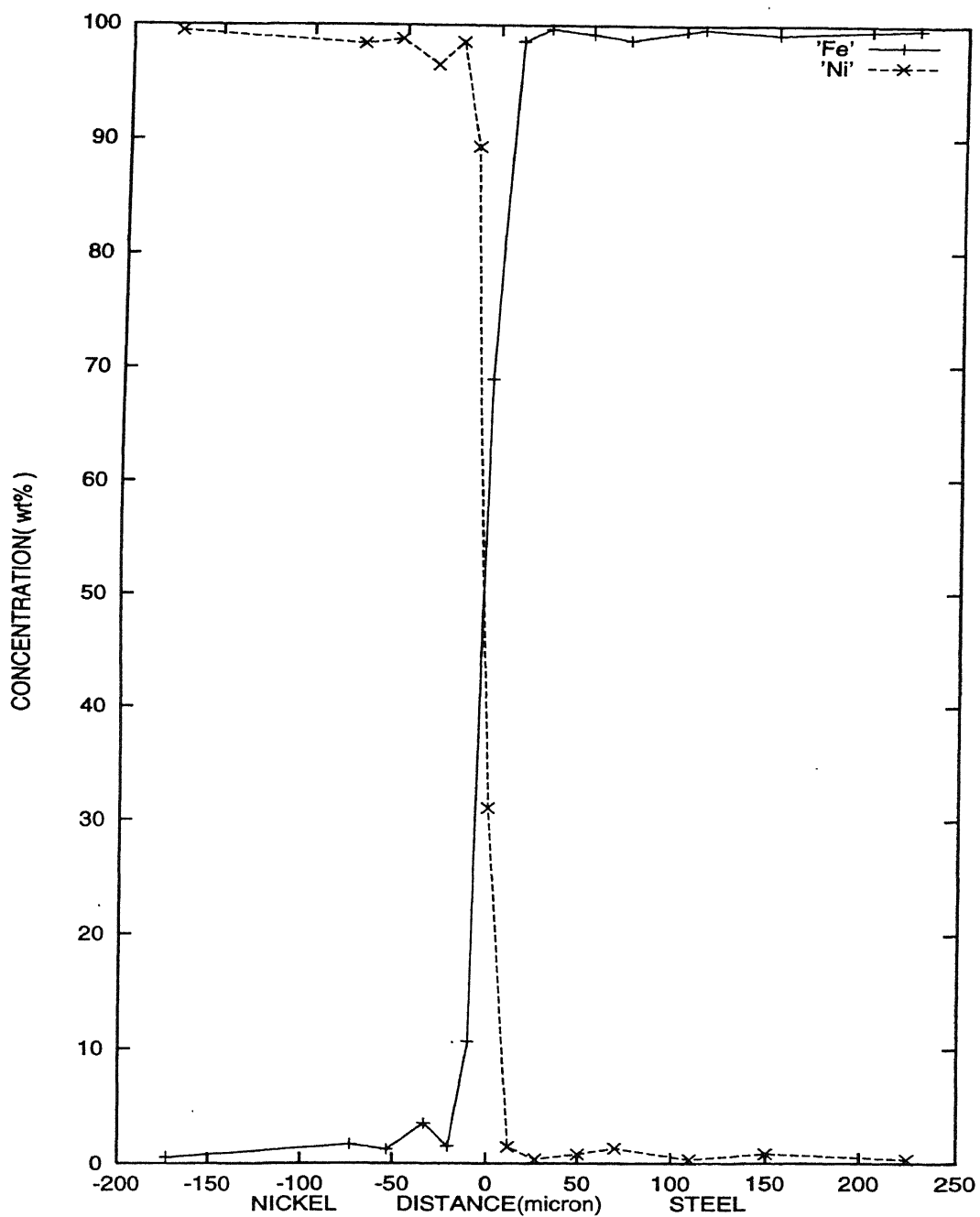
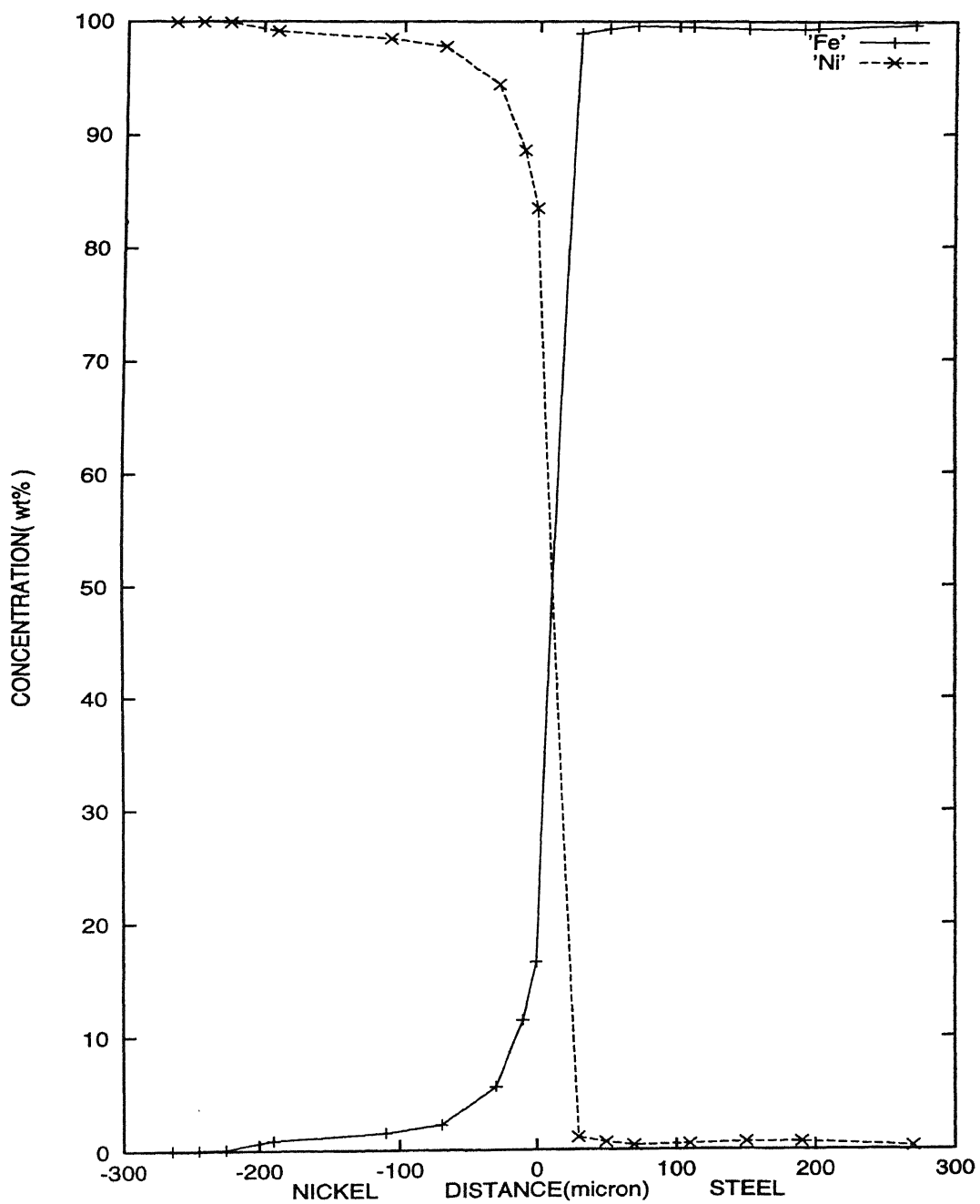Figure 8: Concentration profile of BS Sample in the Interfacial Region

Figure 9: Concentration profile of DS Sample in the Interfacial Region

compaction resulted in densification of nickel layer and also helped in development of interfacial bonds. During subsequent sintering iron diffused deeper into nickel than LS and BS sample, due to more grain boundary and surface diffusion paths generated by compaction.

To examine the influence of hot rolling on the extent of diffusion zones, concentration profile of DS samples with increasing percentage deformation were also determined. Figs. 10, and 11 show the concentration profile for 43% & 56% deformed samples, respectively. The interdiffusion zone thickness for these samples is slightly higher as compared to 70% deformed sample (see Fig. 9). With increase in percentage reduction, the interdiffusion zone thickness is found to decrease. This may be due to reduction in thickness during plastic deformation resulting in successively decreasing interdiffusion zone thickness. Similar trend has been reported elsewhere also [18].

Diffusivity of nickel in iron is approximately 10^{-11} cm^2/sec at 1000^{0}C and 2.5 X 10^{-12} cm^2/sec at 900^{0}C [19]. From this data, a diffusion distance (given by $\sqrt{(Dt)}$) value of approx. 3 μm is obtained for sintering at 1000^{0}C for 15 minutes and approx. 1 μm for reheating time of 40 to 60 minutes at 900^{0}C for hot rolling is obtained. Thus, total diffusion distance of nickel into iron is of the order of 4 μm. Diffusion of iron into clad nickel layer occurs primarily by grain boundary and surface diffusion. Surface and grain boundary diffusivity values of iron in nickel are not known.
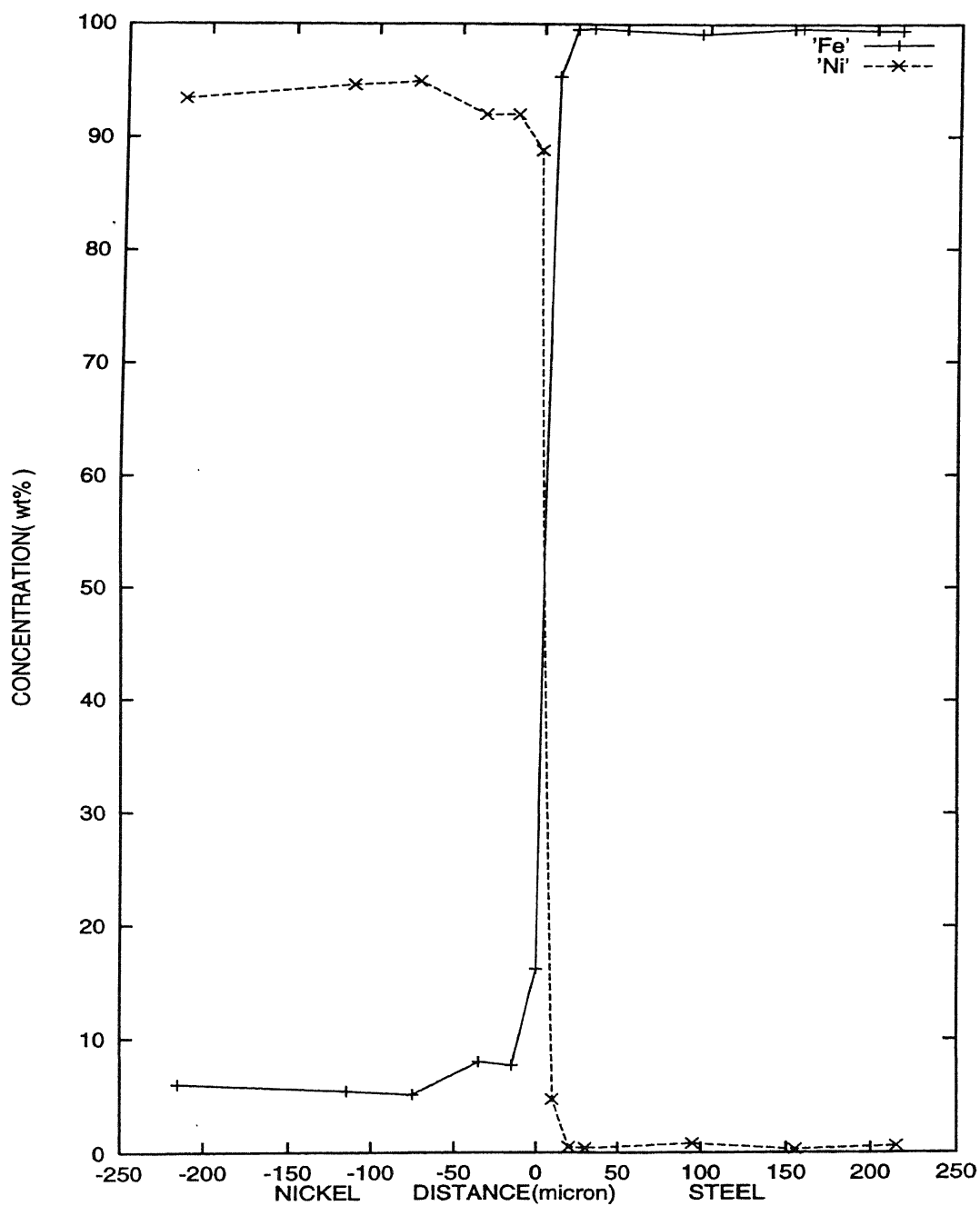
Figure 10: Concentration profile of DS Sample after 43% Reduction
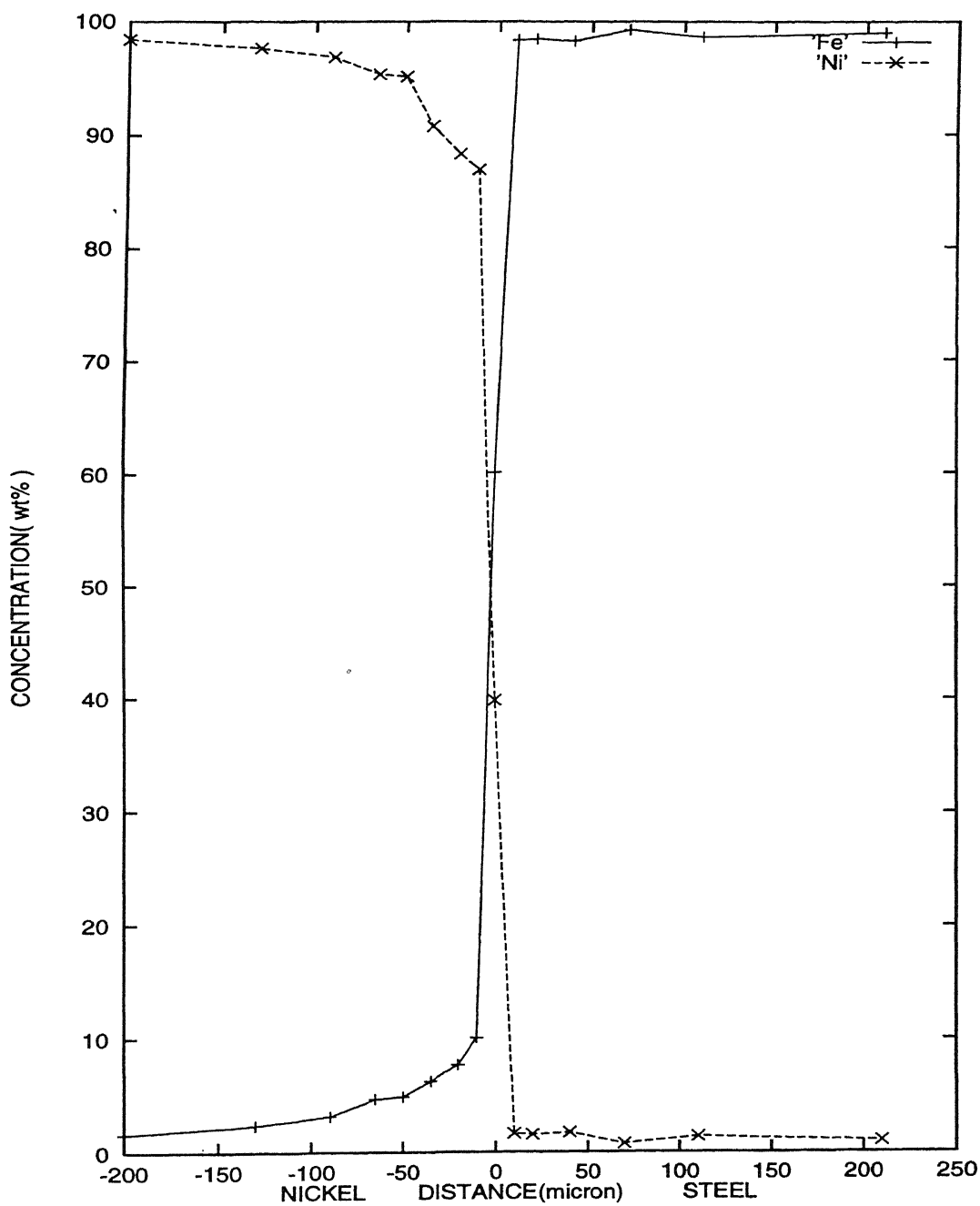
Figure 11: Concentration profile of DS Sample after 55% Reduction

The grain boundary diffusivity of various elements into iron is given by [20],

$$D = 7.6 \times 10^{-8} \times \exp\{ -40350/RT \} \qquad (1)$$

where, gas constant, R = 8.315 J/mole/K.

In the absence of grain boundary diffusion data of iron in nickel, this diffusivity value is used as a first approximation to estimate the extent of diffusion of iron in nickel. A diffusion distance value (given by $\sqrt{(Dt)}$) of approximately 30 μm is obtained for sintering temperature of 1000^{0}C and heating temperature of 900^{0}C for hot rolling. This value is much higher than the diffusion of nickel into iron. Total interdiffusion zone of the order of 33-35 μm is thus obtained. The longer distance travelled by iron to nickel layer is thus due to grain boundary and surface diffusion, which are of relatively higher magnitude.

This may be considered to be in reasonable agreement with the observed experimental data, considering the uncertainty in diffusion data and the fact that effect of hot rolling on diffusion has been ignored.

4.4 Microhardness Data and Analysis

Microhardness profiles of completely hot rolled LS, BS and DS samples, in zones near to interface, are as shown in Figs. 12, 13 & 14, respectively. Average value of hardness of clad nickel layer
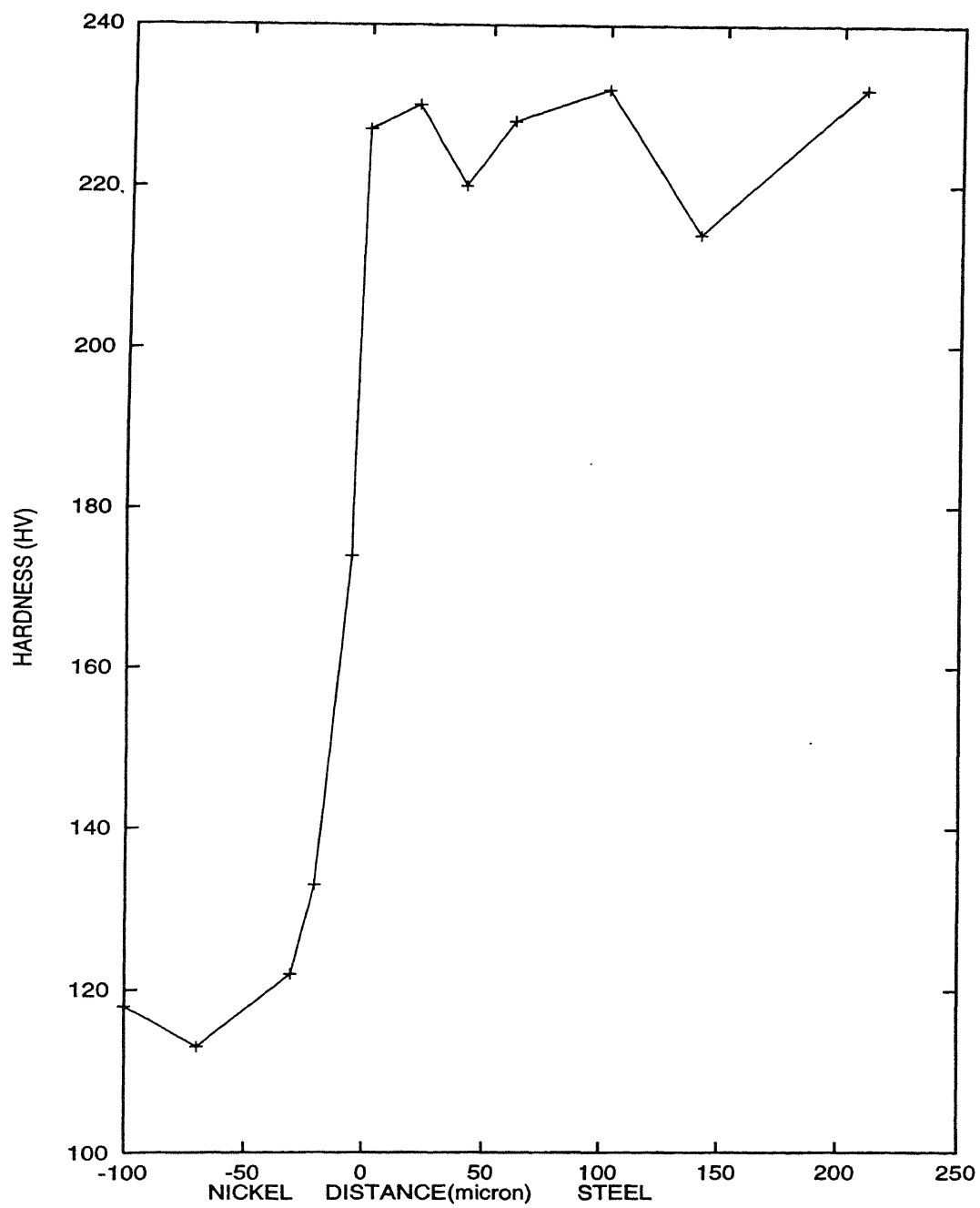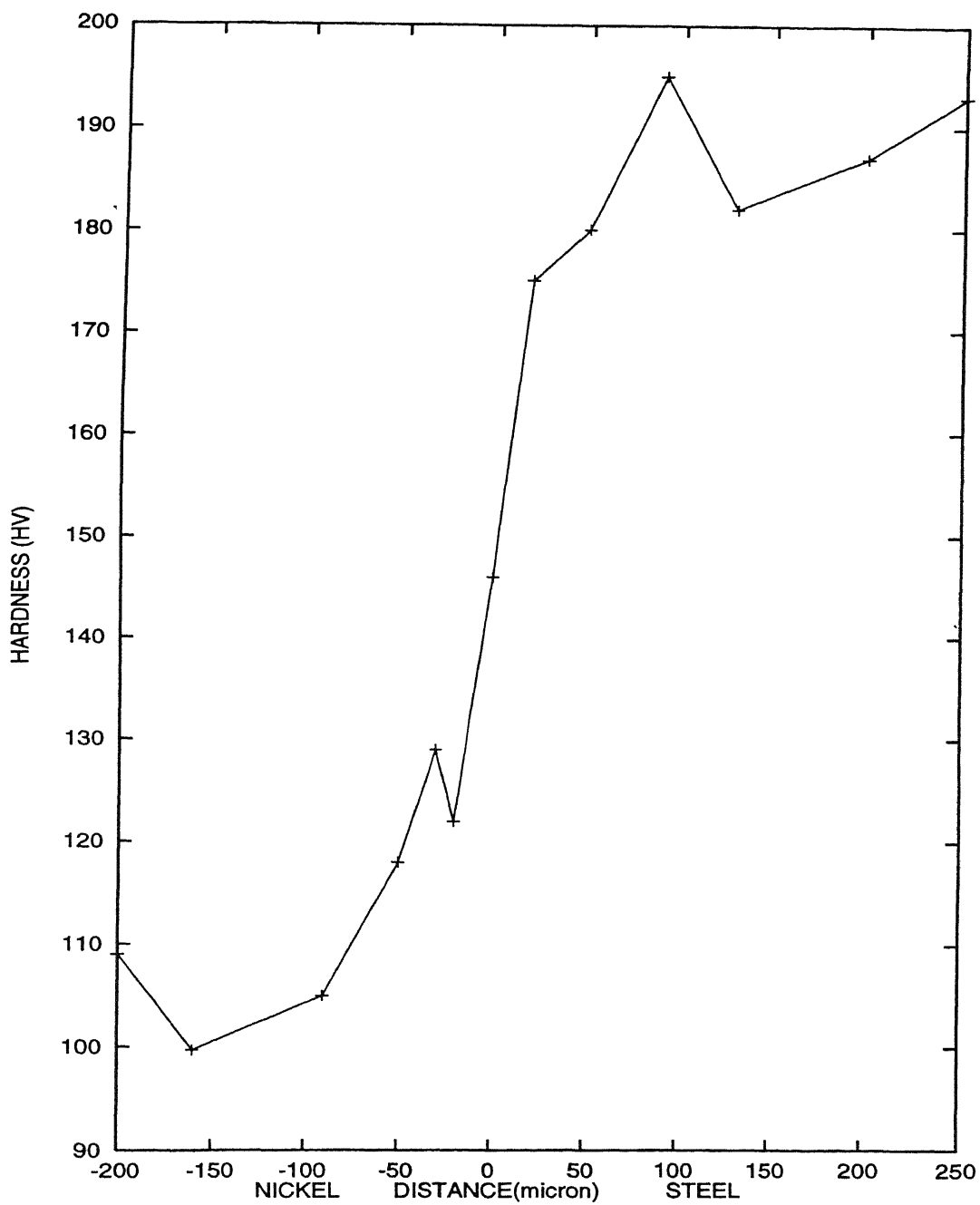
Figure 12: Microhardness profile of LS Sample
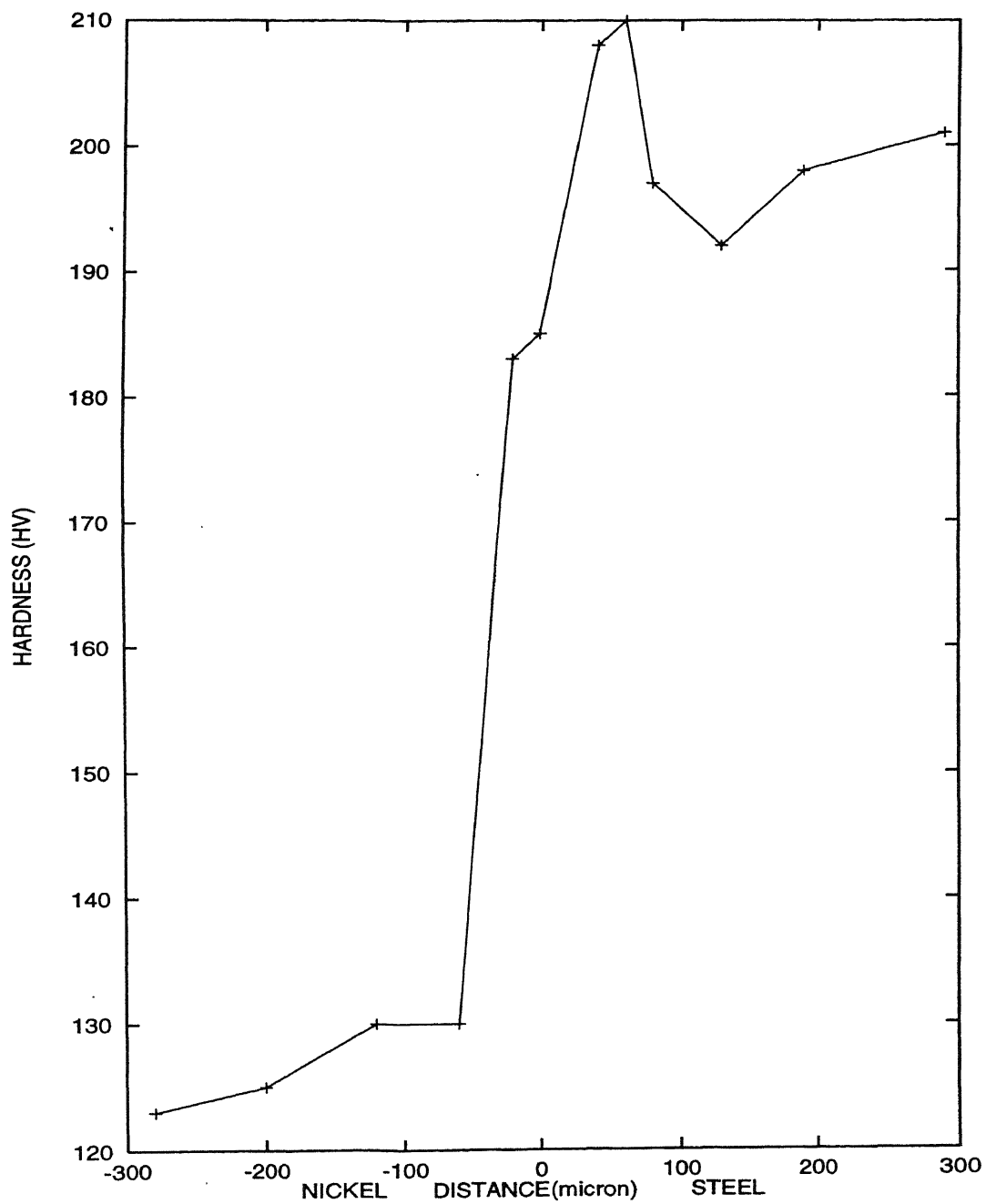
Figure 13: Microhardness profile of BS Sample

Figure 14: Microhardness profile of DS Sample

is found to be 115.5HV, 121.5HV & 127HV respectively. The error in microhardness measurement is 7-10% [21]. These values, are in agreement with the hardness value of wrought nickel reported to be 110-130 HV [22]. Hardness of the clad nickel layer close to interface is higher than at a farther distance from the interface. This is probably due to solid solution strengthening of nickel by iron. The large variation of microhardness on steel side is due to its two phase structure, consisting of soft ferrite and pearlite.

Fig. 15 shows the variation of hardness of clad nickel layer with increasing percentage deformation for DS sample. The hardness of nickel is found to increase with increasing deformation. Higher deformation results in densification of nickel layer and hence its hardness increases.

4.5 Mechanical Testing

Tensile testing of steel and LS sample was done to determine the mechanical properties of composite material. Tensile testing of BS and DS samples could not be carried out as their length was not sufficient for preparation of standard tensile test specimens. The percentage elongation obtained for LS sample is 21.6%. Tensile test values obtained for steel sample and LS sample are given in Table 6. The yield strength and ultimate tensile strength value for nickel as reported in literature are used [23]. On applying the law of mixtures for composite material properties, comparable results are obtained, as observed from Table 6. Thus, the clad composite
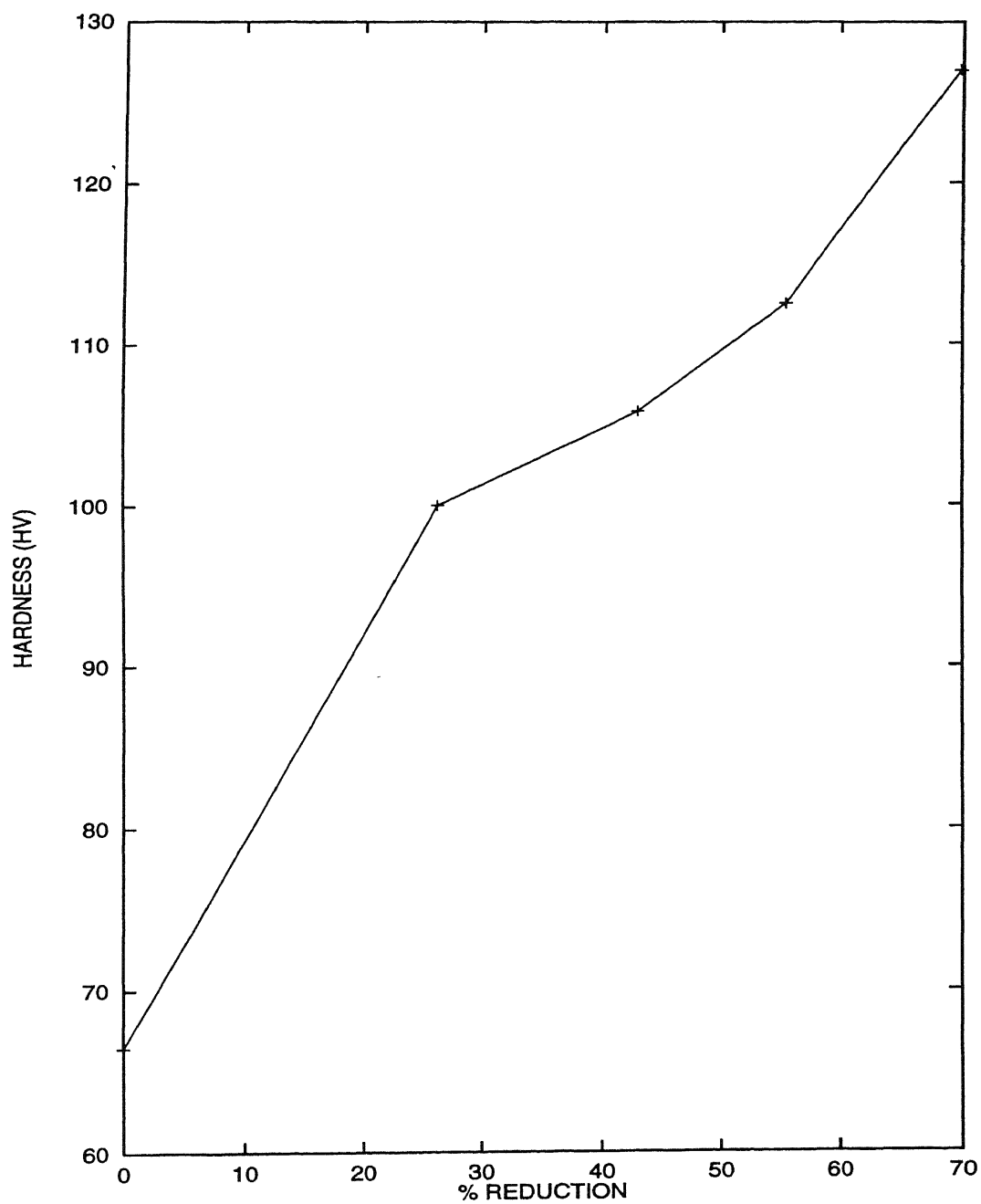
51

Figure 15: Variation of Microhardness with Reduction for DS Sample

Table 6 : Tensile Test data and Composite Material Properties

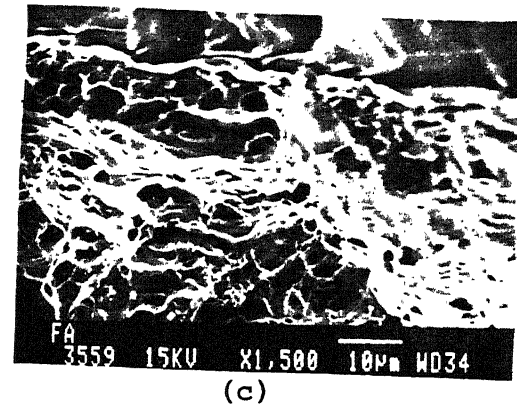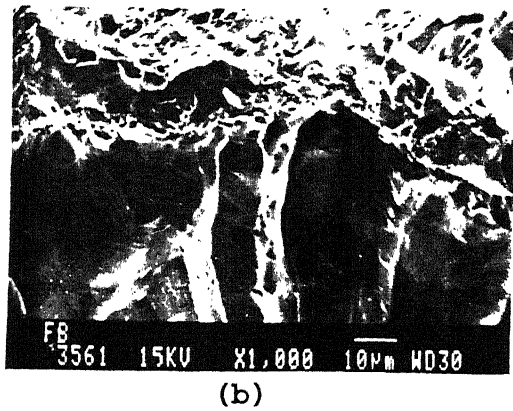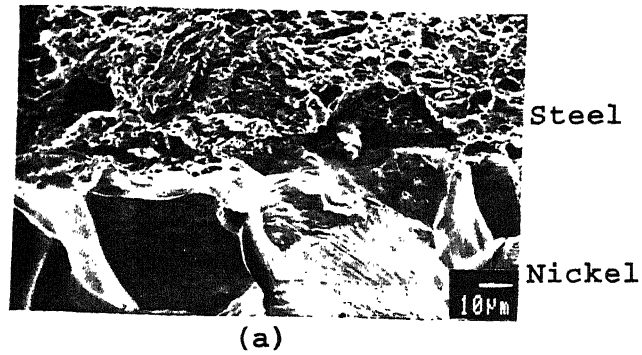| Sample	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)
Steel	312	446
Nickel (From Literature)	148	286
LS Sample	295	442
Law of Mixtures	286	435

(a)

(b)

(c)

Figure 16 : Fractographs of (a) LS Sample, (b) BS Sample and
             (c) DS Sample.

material exhibits the 'composite' mechanical properties, contribution being coming from substrate and base material in proportion to their thickness.

All the samples were tensile loaded unto fracture to determine the nature of fracture. Fractographs of LS, BS and DS samples are shown in Fig. 16 (a), (b) & (c), respectively. From the fractographs, typical dimpled fracture of steel substrate is observed. Clad nickel layer is showing intergranular fracture. Some porosity invariably remained at the grain boundaries, even after large amount of hot deformation and this probably caused intergranular fracture of nickel layer. Delamination of the interface region has not occurred in any of the samples. This shows the strong nature of bonds formed at the interface.

4.6 Comparison of Various Routes

For obtaining nickel clad steel composite material, three different routes consisting of different powder preplacing techniques were followed in the present work. The route which is economically attractive and industrially suitable is proposed to be via use of slurry of nickel powder and organic binder. This route can be designed to produce continuous nickel clad steel composite material. On steel sheet, slurry can be poured and levelled to required thickness. This can be passed through a continuous sintering furnace and interlinked rolling mill. Automation can easily be achieved in this case.

The major disadvantage of loose powder route is the difficulty in handling of the loose powder. The die compacted route has the costly and additional die compaction step involved with it. Moreover, the interdiffusion zone in this case is higher and it may restrict the 'useful' thickness of the clad layer.

CHAPTER 5

Conclusions

1. Nickel cladding on medium carbon steels has been successfully obtained by using nickel powder as clad layer and steel sheet as substrate via hot rolling. The nickel powder is preplaced on rough steel surface by three different techniques viz., i) as loose powder, ii) by using organic binder, and iii) as die compacted powder. Optimum processing route consists of, i) Sintering of all the samples for 15 minutes at 1000^0C, & ii) Hot rolling in 4-7 steps to total reduction of nearly 65 to 70% reduction.

2. Microstructural evaluation has indicated that a good metallurgical bond has developed at the steel/nickel interface. Interfacial contamination, porosity etc. is not observed.

3. The interdiffusion of iron and nickel at the interface has occurred in approximately 25-40 μm zone in case of loose and bindered powder route, while for die compaction route zone thickness is twice this value. Iron has diffused to longer distance in clad nickel layer as it followed surface and grain boundary diffusion as compared to diffusion of nickel to iron, which primarily occurred by slower matrix diffusion.

4. Microhardness of clad nickel layer is found to increase with increasing percentage reduction. Microhardness value of clad nickel layer is in range 115-127 HV for fully dense composite material. This is in agreement with value for wrought nickel

reported to be 110-130 HV.

5. Overall macroscopic strength of clad composite material essentially followed the law of mixtures i.e. combined strength characteristics of base steel and clad nickel layer in proportion to their thickness. Fractographs of tensile fractured samples showed a typical dimpled fracture of base steel and intergranular fracture of the clad nickel layer. The interface between steel and nickel has not delaminated, thereby indicating good cohesive strength of the interface.

6. The cladding route which is economical and suitable for industrial exploitation has been found to be via use of slurry of organic binder and nickel powder being preplaced on steel substrate followed by sintering and hot rolling.

CHAPTER 6

Suggestions for Future Work

1. Die compaction has resulted in higher relative density of porous nickel layer in the present study. Application of temperature along with compaction can yield very good results and this will make an excellent study for future work. It will also be interesting to find if hot rolling can altogether be avoided.

2. Cladding of nickel alloys like Inconel, Hastealloy, Monel etc. having wide applications can be studied.

3. The cohesive strength of clad bond needs to be determined. A device for this purpose can be developed as described in [5].

References

[1] N. Bay et al, *J. Mater. Process. Tech.*, **45**, 1994, p 1.

[2] L. R. Vaidyanath and D. R. Milner, *Brit. Weld. J.*, **7**, No.1, 1960, p 1.

[3] K.J.B. McEwan and D. R. Milner, *Brit. Weld. J.*, **9**, No. 7, 1962, p 406.

[4] S.H. Gelles, Interactions Between Core and Cladding, Nuclear and Reactor Fuel Elements, ed. A.R. Kaufmann, Interscience Pub., New York, 1962.

[5] V. M. Ocheretyanskii And A. V. Aleshina, *Porosh. Met.*, No. 11, Nov 1986, p 85.

[6] Yu.M. Korolev, Manufacturing of Nickel Clad Molybdenum Sheets, Int. Conf. On Pow. Met. and Related High Temperature Mat., ed. P. Ramakrnam, Trans Tech Pub., 1987.

[7] Jun-ichi Echigoya, Principles of Adhesion Testing, Handbook of Advanced Materials Testing, ed. P. Cheremisinoff, Marcel Dekker Inc., New York, 1995.

[8] V.P. Katashinskii, *Porosh. Met.*, No. 9, Sept 1987, p 17.

[9] V.A. Maslyuk et al, *Porosh. Met.*, No. 8, Aug 1991, p 35.

[10] F.W Heck et al, Proc. of the 20th Annual Meeting, Metal Powder Industries Federation, 1964, p 202 as cross reference from [23].

[11] R.M. German, Powder Metallurgy Science, Metal Powder

Industries Federation, 1994.

[12] A.V. Lyushinskii et al, *Porosh. Met.*, No. 4, April 1991, p 20.

[13] R. K. Dube and P. K. Bagdi, *Met. Trans. A*, **24 A**, Aug. 1993, p 1753.

[14] I.I. Renne, *Porosh. Met.*, No. 3, March 1988, p 26.

[15] I.I. Renne, *Porosh. Met.*, No. 11, Nov. 1986, p 8.

[16] B. Lopez, *Mat. Sci. & Tech.*, **12**, Jan. 1996, p 45.

[17] R.F. Tylecote, *Brit. Wel. J.*, **1**, No. 3, 1954, p 117.

[18] A.G. Mamalis et al, *J. Mater. Process. Tech.*, **45**, 1994, p 407.

[19] W.H. Wöhlbier, Diffusion and Defect Data, **8**, No. **1-4**, Trans Tech Pub., Ohio, 1974.

[20] J. Fridberg et al, *Jernkout. Ann.*, **153**, p 263.

[21] W.Riedel, Electroless Nickel Plating, Finishing Pub. Co.,1991.

[22] D.S. Clark and W.R. Varney, Physical Metallurgy for Engineers, D. Van Nostrand Co., New York, 1965.

[23] S.J. Rosenberg, Nickel and Its Alloys, National Bureau of Standards Monograph, U.S., 1968.